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OLAVI ERÄMETSÄ and KAJ KARLSSON

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THE CRYSTAL CHEMISTRY OF SOME SODIUM POLYSULPHIDES

by

OLAVI ERÄMETSÄ and KAJ KARLSSON

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CONTENTS

The investigation comprises the preparation in ethanolic solution of some waterfree sodium polysulphides, and determination of the unit cell dimensions of α-Na_2S_2, β-Na_2S_2 and Na_2S_4.

Many research workers have devoted their attention to the preparation and the constitution of sodium polysulphides, but even today the existence of some of the polysulphides remains to be proved. Below is given a brief review of papers concerned with waterfree sodium polysulphides.

Sodium disulphide

Waterfree sodium disulphide was prepared by RULE & THOMAS [1] by reducing an absolute ethanolic solution of sodium tetrasulphide with an excess of metallic sodium. BERGSTROM [2] prepared the disulphide by reaction between sodium and sulphur in liquid ammonia, but did not isolate the disulphide. No details have been given. FEHER & BERTHOLD [3] repeated the experiments of RULE & THOMAS [1], to obtain a similar result. They reported that those preparations dried at room temperature contained on an average 4 ··· 6 % ethanol, and discussed the possibility of an alcoholate $9Na_2S_2 \cdot 2C_2H_5OH$. However, they established, that an alcoholate is not formed, because preparations dried either at room temperature or at 150 ^{o}C have the same X-ray pattern. Furthermore, FEHER & BERTHOLD prepared the disulphide in liquid ammonia. The authors described the product and gave DEBYE-SCHERRER-patterns; these demonstrated that two modifications exist, a low temperature modification α-Na_2S_2, obtained only from ethanolic solution, and a high temperature modification β-Na_2S_2.

Sodium trisulphide

LOCKE & AUSTELL [4] prepared sodium trisulphide by reaction between sodium and sulphur in boiling toluene, and, independent of the proportions of sodium and sulphur, always obtained products with Na : S = 2 : 3. DRAVES & TARTAR [5] and PEARSON & ROBINSON [6] confirmed this finding. FRIEDRICH [7] investigated the composition diagram for the system Na_2S - S, and obtained a maximum at composition Na_2S_3, wheras at the same point THOMAS & RULE [8] obtained only a crack. Conversely, PEARSON & ROBINSON [6] obtained neither a crack nor a maximum. Neither did they obtain sodium trisulphide by splitting off sulphur from higher polysulphides at temperatures of some hundreds of degrees, but obtained disulphide, tetrasulphide and pentasulphide. Microscopic examinations of polysylphides which correspond to the composition Na_2S_3, prepared from meltings, showed a typical perlite structure, indicating the existence of eutectic mixtures. Their conclusion was that trisulphide is formed at relatively low temperatures (e. g. in boiling toluene at 110 ^oC), but decomposes at higher temperatures in disulphide and tetrasulphide. On trying to prepare sodium trisulphide from sodium and sulphur in boiling toluene, FEHER & BERTHOLD [3] always obtained products with the composition $Na_2S_{3.3}$ -- $Na_2S_{3.5}$. By melting $Na_2S_{3.5}$ which had been prepared in this way with the calculated amount of sodium, the result was a product $Na_2S_{3.0}$, which proved on X-ray examination to be an equivalent mixture of sodium disulphide and sodium tetrasulphide. FEHER & BERTHOLD [3] also tried to prepare trisulphide in liquid ammonia, in a way similar to that employed for sodium disulphide. They obtained a product Na_2S_3, which was a mixture of disulphide and tetrasulphide. From this, they concluded that a composition Na_2S_3 does not exist, especially as ZINTL & al. [9], by potentiometric titration of higher polysulphides in liquid ammonia with sodium, have only once obtained potential jumps for trisulphide.

Sodium tetrasulphide

RULE & THOMAS [1] prepared sodium tetrasulphide by the transference of concentrated sodium ethylate solution into a sodium hydrogen sulphide solution by saturating with hydrogen sulphide, and adding the calculated amount of sulphur. After the sulphur had dissolved, the alcohol was distilled of, by which means the sodium tetrasulphide was separated. PEARSON & ROBINSON [6], as well as FEHER & BERTHOLD [3], have confirmed this..The last mentioned authors discuss the possibility of this method giving an alcoholate with the composition $2Na_2S_4 \cdot C_2H_5OH$, but they do not think this is likely, because the very low alcoholic content in the preparations points to occluded alcohol. They also determined some physical properties for the tetrasulphide and DEBYE-SCHERRER-patterns. BERGSTROM [2] prepared the tetrasulphide in liquid ammonia, but did not obtain a product which was completely free of ammonia. Sodium tetrasulphide has a noticable maximum in the

melting diagram Na_2S - S, and is thus considered to be the most stabile sodium polysulphide.

Sodium pentasulphide

HUGOT [10] reported on having prepared sodium pentasulphide from the elements in liquid ammonia, but FEHER & BERTHOLD [3] doubt this. All authors who have investigated the preparation of sodium pentasulphide state that it cannot be obtained in a pure form from ethanolic solution. Nevertheless, the existence of the compound has been proved by thermic investigations of the system Na_2S - S, made by THOMAS & RULE [8], as well as by PEARSON & ROBINSON [6]. So far, the only way in which sodium pentasulphide has been made, is by melting a lower polysulphide with sulphur. KLEMM & al. [11] melted sodium monosulphide with the calculated amount of sulphur in an evacuated tube. PEARSON & ROBINSON [6] used Na_2S_3, while FEHER & BERTHOLD [3] used sodium disulphide as well as sodium tetrasulphide. The last mentioned authors also gave X-ray patterns for sodium pentasulphide, and reported on other physical properties.

Experimental

The syntheses were made in a 250 ml three-necked flask, fitted with a refluxer and a gas delivery tube. The flask was heated with an electric heating mantle. All the syntheses were made in a N_2-atmosphere. The nitrogen was purified by passing it through solid sodium hydroxide, calcium chloride and activated charcoal, and following this the oxygen was burned off with copper in an oven as described by MEYER & RONGE [12].

The sodium and α-sulphur used were RIEDEL de HAËN "Chemisch rein" and "Chemisch rein, krystallisiert", respectively. RIEDEL de HAËN's "Fixanal" solutions were used for titrimetric determinations. The μ-sulphur was made from ammonium polysulphide and sulphur monochloride (S_2Cl_2, BDH p. A.) The chemical analysis of the polysulphide preparations were made titrimetrically, as described by FEHER & BERTHOLD [13]. The limits of error were about ± 2 ··· 3 %.

The X-ray powder patterns were taken by a NORELCO geiger counter diffractometer, using CuK_α radiation.

Sodium disulphide

Sodium disulphide was prepared by a method described by RULE & THOMAS [1] in which a sodium tetrasulphide solution in absolute ethanol was reduced with an excess of metallic sodium to a disulphide difficult to dissolve. The disulphide was

Fig. 1. α-Na_2S_2. Magnification 36 x. (Black background used).

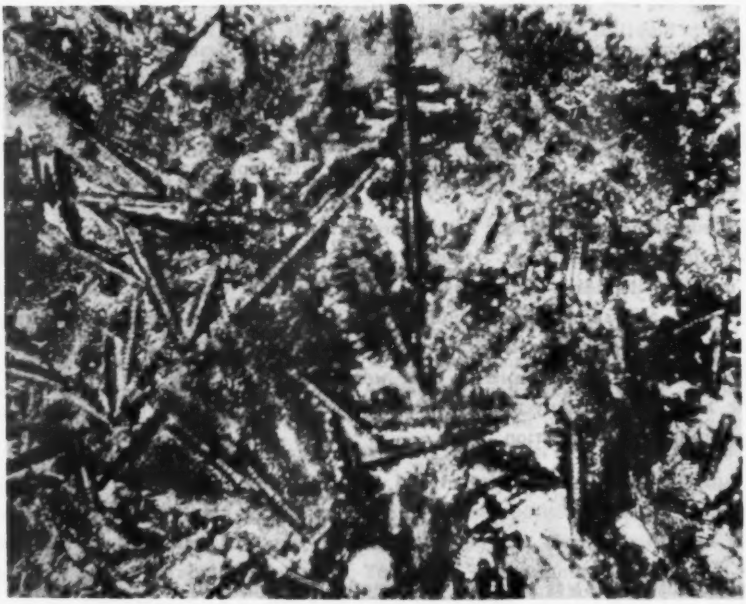

Fig. 2. β-Na_2S_2. Magnification 120 x.

filtered off, washed with some absolute ethanol, and dried in vacuo over P_2O_5. These and all the succeeding operations were carried out in an N_2-atmosphere. If large amounts of ethanol were used for washing, white patches appeared on the surface of the precipitate; this was also noticed by RULE & THOMAS [1].

To investigate these phenomena, some disulphide was boiled in ethanol. It dissolved, but on cooling and evaporating the solution, a white substance precipitated, which gave off H_2S on reaction with acid. X-ray diffraction patterns showed it to be amorphous. Publications state that Na_2S is either amorphous or cubic, and thus the substance may probably have been the monosulphide.

The ratio of sodium to sulphur in the prepared disulphide was always on the low side. RULE & THOMAS [1] and FEHER & BERTHOLD [3] also observed this. They assumed it to depend upon the fact that small quantities of tetrasulphide separate out with the disulphide owing to the salting-out action of the sodium ethylate produced by the reaction. However, a crystal structure determination showed the salt to be mainly Na_2S_2.

Sodium disulphide is a bright yellow, microcrystalline and very hygroscopic powder. According to FEHER & BERTHOLD [3], it exists in two modifications, a low temperature modification α-Na_2S_2, and a high temperature modification β-Na_2S_2. The modification change takes place in the temperature interval 150 °C ··· 250 °C, and is irreversible. FEHER & BERTHOLD [3] obtained the α-Na_2S_2 only from ethanolic solution, whereas the product from liquid ammonia had to be heated to 300 °C in order to lose all the occluded NH_3. In this work, a salt was obtained by melting the synthetised disulphide in vacuo. Microscopic and X-ray examinations proved it to have a crystal structure other than the original. This β-Na_2S_2 was always a slightly darker yellow than the α-Na_2S_2. By heating α-Na_2S_2, prepared in ethanol, in vacuo, to 150 °C, FEHER & BERTHOLD [3] obtained products which were olive green, while the products obtained from liquid ammonia were yellow.

When an ethanolic solution of Na_2S_2, saturated at 25 °C, was kept for several weeks at a temperature of 20 °C, crystals about $\frac{1}{2}$ ··· 1 mm long were obtained (Fig. 1). Examined under a polarisation microscope, these crystals showed that α-Na_2S_2 is monoclinic or triclinic.

Microscopic preparations of β-Na_2S_2 were made by washing β-Na_2S_2 with ethanol, and re-melting it between preparation slides. These preparations (Fig. 2) showed that β-Na_2S_2 has a straight or almost straight extinction. When the β-Na_2S_2 was not washed, preparations with more than one kind of crystal resulted (Fig. 3).

X-ray examination

Qualitative comparison of the powder patterns of sodium disulphide obtained in this investigation and those of FEHER & BERTHOLD [3] and KLEMM & al. [11], showed that they were all almost identical.

The powder patterns of α-Na_2S_2 and β-Na_2S_2 are shown in Fig. 4 and Fig. 5, and their interpretation in Table 1 and Table 2, respectively.

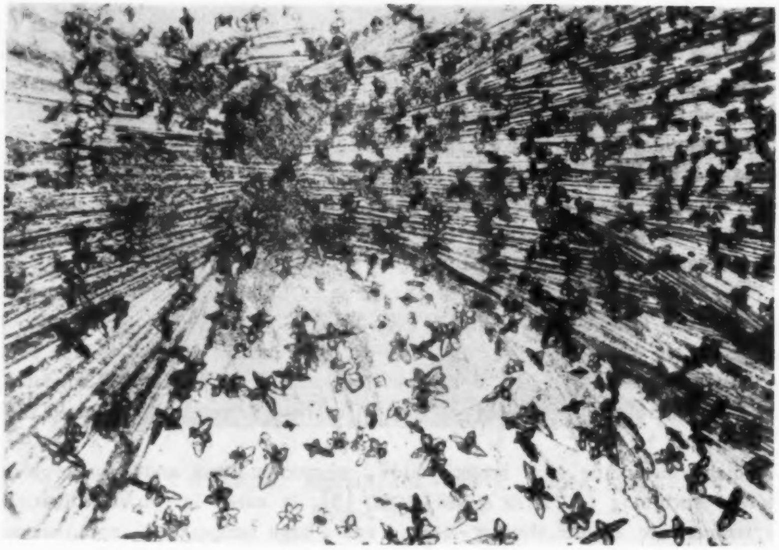

Fig. 3. Unpure β-Na_2S_2. Magnification 120 x.

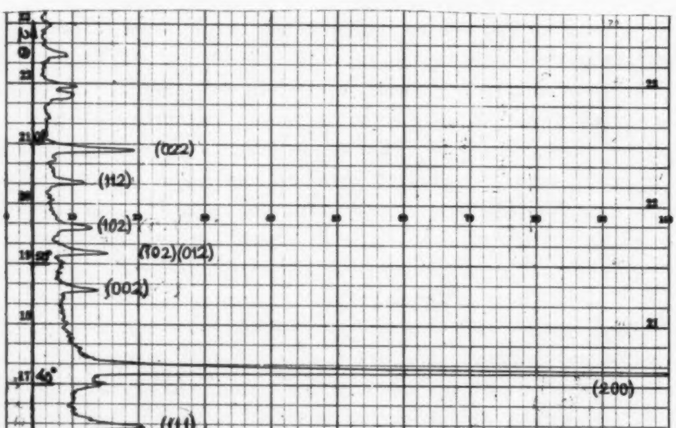

Fig. 4. X-ray pattern of α-Na_2S_2.

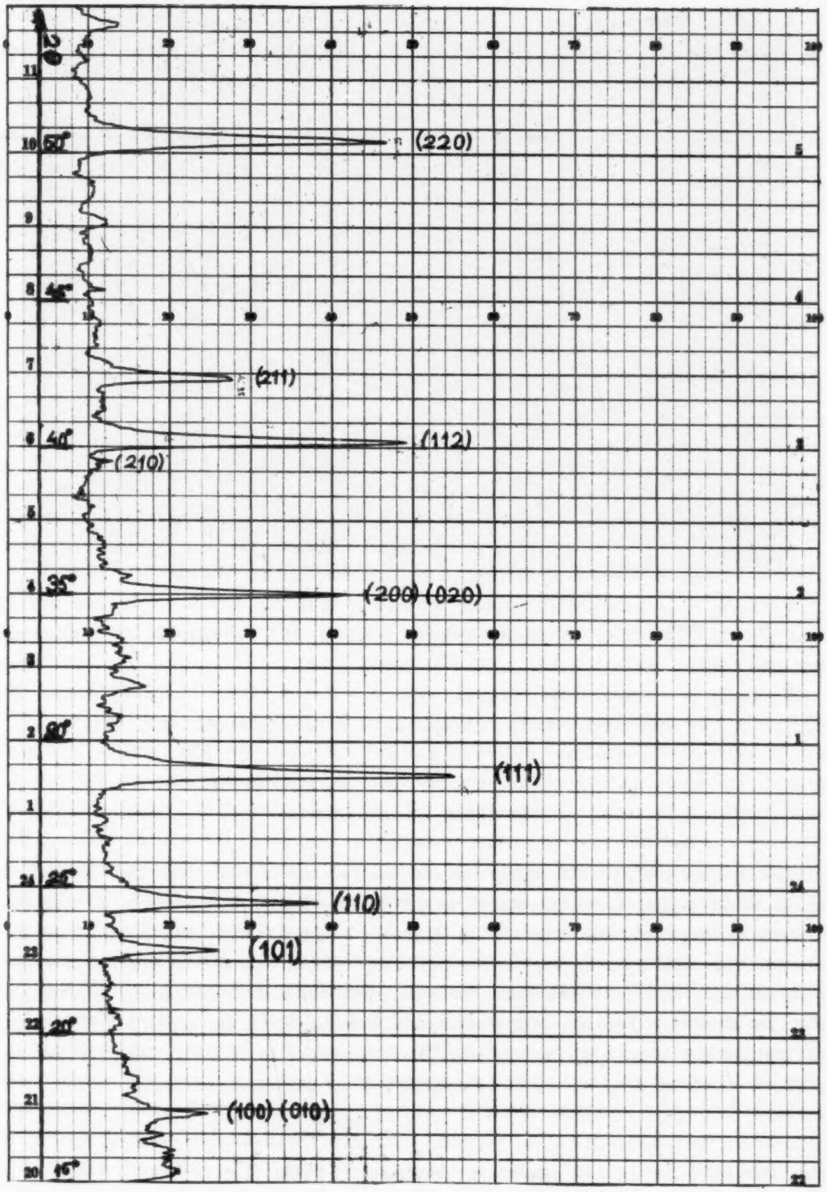

Fig. 5. X-ray pattern of β-Na_2S_2.

Table 1.
Interpretation of the powder pattern of α-Na_2S_2.

2θ [°]	d_{hkl} [Å]	hkl		I %
23.30	3.81_3		001	68
28.70	3.10_0		011	57
31.90	2.80_0		101	
36.30	2.47_8		111	
41.00	2.20_0		200	100
47.73	1.90_5		002	
50.85	1.79_3	$\bar{1}02$	012	
52.95	1.72_5		102	
56.50	1.62_5		112	
59.40	1.55_2		022	

Table 2.
Interpretation of the powder pattern of β-Na_2S_2.

2θ [°]	d_{hkl} [Å]	hkl		I %
17.35	5.10_6	100	010	
23.00	3.86_6	101		
24.60	3.61_0	110		
29.00	3.08_0	111		100
35.15	2.55_2	200	020	
39.20	2.29_5	210		
40.30	2.24_0	112		93
42.35	2.13_7	211		
50.65	1.80_4	220		85

α-Na_2S_2 is a monoclinic crystal with: a = 4.40 Å, b = 5.33 Å, c = 3.81 Å and β = 93° 12′. The measured density 2.01 g/cm^3 corresponds to 1 molecule per unit cell.

β-Na_2S_2 is a monoclinic crystal with: a = b = 5.11 Å, c = 5.76 Å and β = 88° 44′. The measured density corresponds to 2 molecules per unit cell.

Sodium trisulphide

The synthesis of sodium trisulphide was carried out in the same way as the synthesis of tetrasulphide. A calculated amount of μ-sulphur was added to a saturated sodium hydrogensulphide solution in absolute ethanol. After the sulphur had dissolved, the solution was boiled for one hour. About 4/5 of the ethanol was then distilled off. The separated crystals were primarily sodium tetrasulphide, thus showing that the synthesis had not been successful. Nor did RULE & THOMAS [1] succeed in making the trisulphide in this way. It is therefore most likely that, if the trisulphide exists at all, it cannot be synthetised in ethanolic solution.

Sodium tetrasulphide

Sodium tetrasulphide was prepared according to a method described by RULE & THOMAS [1]. A sodium hydrogen sulphide solution was prepared by saturating a

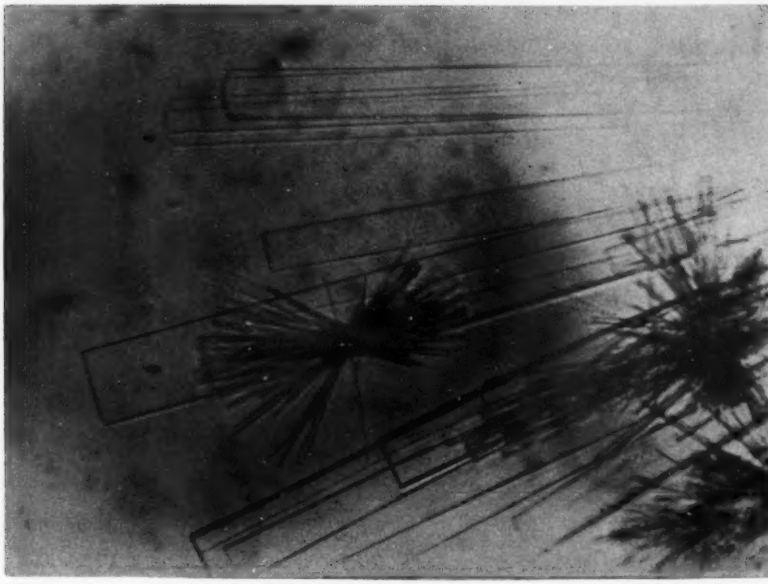

Fig. 6. Na_2S_4 in (010). The crystals are defined by (100) and (001). nification 120 x.

waterfree sodium ethylate solution with dry hydrogen sulphide. The excess of the gas was subsequently removed by heating the solution to boiling point and passing through it a stream of N_2. To form Na_2S_4, a calculated amount of α-sulphur was added. After boiling for about one hour, the solution was concentrated to about 1/5 of its original volume by vacuum distillation. The separated crystalline product was filtered off, washed with a small amount of absolute ethanol, and dried in vacuo over P_2O_5. Chemical analysis showed the product to have the composition Na_2S_4.

Sodium tetrasulphide is an orange yellow, crystalline and very hydroscopic powder, which easily dissolves in absolute ethanol. According to FEHER & BERTHOLD [3], it recrystallises as Na_2S_4. RULE & THOMAS [1] obtained products with "a curious olive green tinge". The present authors, by melting and recrystallising the tetrasulphide obtained the same X-ray pattern as for the original product. The recrystallised product was always orange yellow. FEHER & BERTHOLD [3] also obtained an orange yellow tetrasulphide, but after melting and recrystallisation it became olive green. However, they found the same X-ray pattern before and after melting.

The preparations for microscopic examination were made by cooling a hot, saturated tetrasulphide solution on preparation slides. As a rule the tetrasulphide crystallises in spherolites (Fig. 6). The different crystals in the spherolites had an

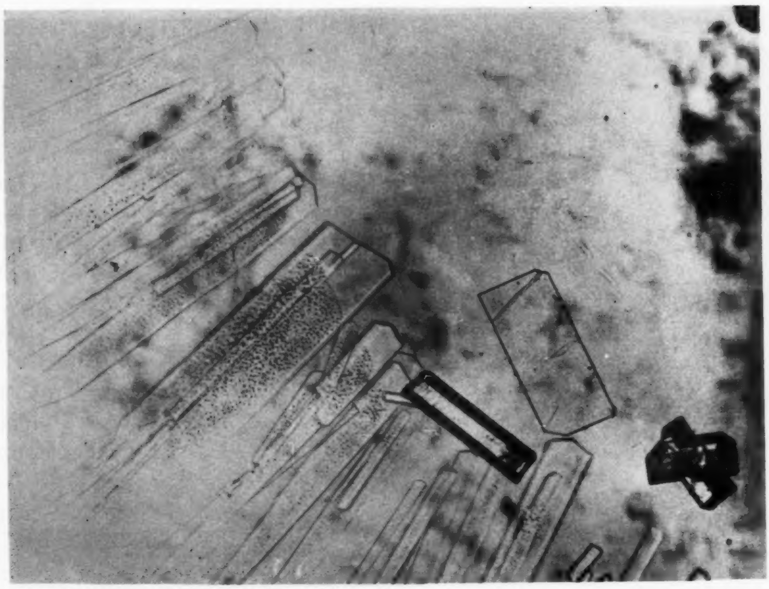

Fig. 7a. Na_2S_4 in (010). The picture explained in Fig. 7b. Magnification 120 x.

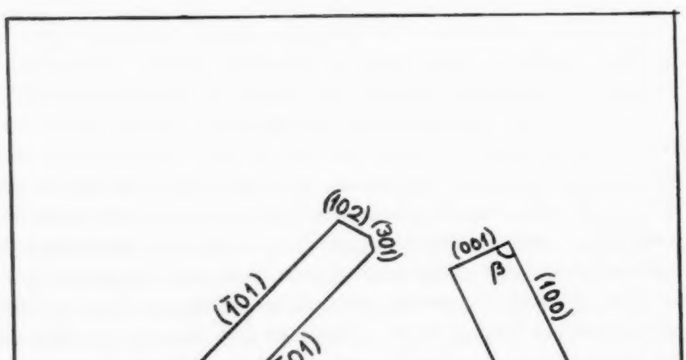

Fig. 7b. Na_2S_4 in (010). Explanation to Fig. 7a.

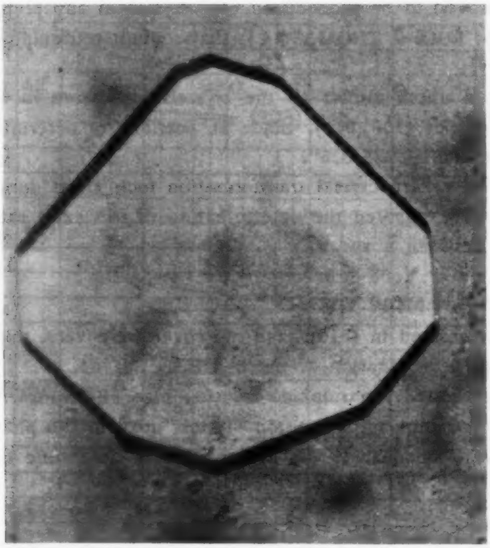

Fig. 8a. Na_2S_4 in (010) after crystal transformation. Magnification 320 x.

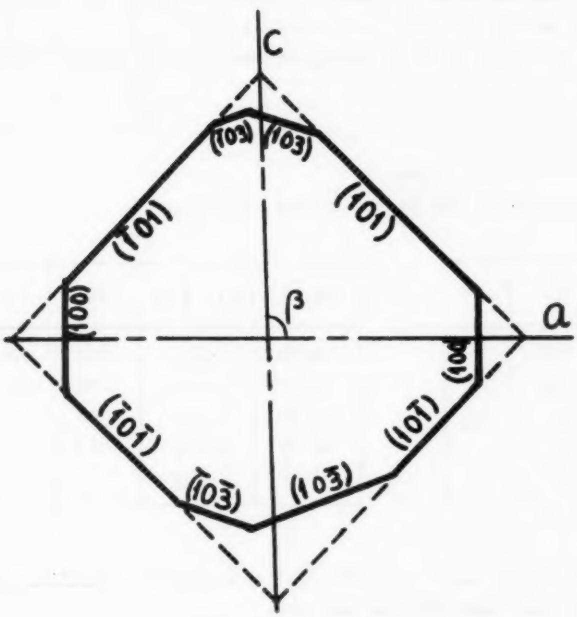

Fig. 8b. Na_2S_4 in (010). Explanation to Fig. 8a.

almost straight extinction, and proved to be monoclinic. No crystal in any preparation confirmed the statement of RULE & THOMAS [1], that sodium tetrasulphide crystallises in cubic symmetry.

In one preparation (Fig. 7), in which almost all the crystals had grown in direction (101), one crystal, defined by (100)(001), made it possible to determine the angle between a- and c-axis as $91.5^{o} \pm 0{,}5^{o}$.

In another preparation (Fig. 8), where crystal transformation took place during 24 hours, crystals were formed which enabled the determination of the axial ratio c : a, and to confirm the angle between a and c.

$$c : a = 1.08 \pm 0.05$$
$$\beta = 91.1^{o} \pm 0.5^{o}$$

As the crystals were always orientated in (010), and moreover were very thin, it was impossible to arrive at any determination of the b-axis.

By keeping for some weeks a saturated tetrasulphide solution in equilibrium with a small amount of CS_2, about 1.5 mm thick mosaic crystals grew in the phase boundary. Because the crystals were opaque, it was not possible to determine the b-axis from these either.

X-ray examination

A qualitative comparison between the powder patterns obtained and those of FEHER & BERTHOLD [3] showed that they were almost identical.

The powder pattern of Na_2S_4 is shown in Fig. 9 and its interpretation in Table 3.

Table 3.
Interpretation of the powder pattern of Na_2S_4.

2θ [°]	d_{hkl} [Å]	hkl	I %
20.10	4.41_0	002	
22.20	3.99_7	200	59
24.20	3.66_5	$\bar{2}01$	
24.60	3.61_5	201	
29.20	3.04_0	022	
31.00	2.88_0	220	100
33.45	2.67_6	300	82
39.60	2.27_2	203	
40.80	2.20_8	004	
41.10	2.19_2		

Na_2S_4 is a monoclinic crystal with: a = 8.01 Å, b = 8.24 Å, c = 8.82 Å and $\beta = 91^{o}\,5'$. There are four molecules per unit cell.

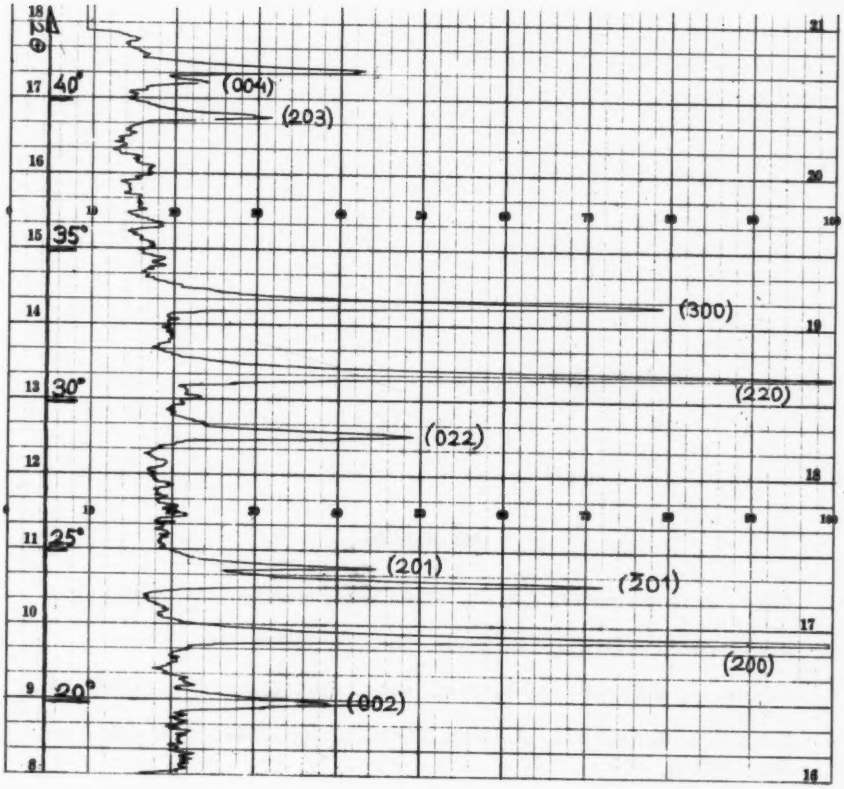

Fig. 9. X-ray pattern of Na_2S_4.

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